



THE UNIVERSITY *of* EDINBURGH

## Edinburgh Research Explorer

### Characterisation of waste water from biomass gasification equipment: a case-study from Cambodia

**Citation for published version:**

Shackley, S 2015, 'Characterisation of waste water from biomass gasification equipment: a case-study from Cambodia', *World Review of Science, Technology and Sustainable Development*, vol. 12, no. 2, pp. 126-151 . <https://doi.org/10.1504/WRSTSD.2015.073829>

**Digital Object Identifier (DOI):**

[10.1504/WRSTSD.2015.073829](https://doi.org/10.1504/WRSTSD.2015.073829)

**Link:**

[Link to publication record in Edinburgh Research Explorer](#)

**Document Version:**

Peer reviewed version

**Published In:**

World Review of Science, Technology and Sustainable Development

**General rights**

Copyright for the publications made accessible via the Edinburgh Research Explorer is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

**Take down policy**

The University of Edinburgh has made every reasonable effort to ensure that Edinburgh Research Explorer content complies with UK legislation. If you believe that the public display of this file breaches copyright please contact [openaccess@ed.ac.uk](mailto:openaccess@ed.ac.uk) providing details, and we will remove access to the work immediately and investigate your claim.



# Characterisation of Waste Water from Biomass Gasification Equipment: A Case-Study from Cambodia

Simon Shackley  
School of GeoSciences  
University of Edinburgh  
EH8 9XP  
Edinburgh, UK  
simon.shackley@ed.ac.uk

## Abstract

The gasification of rice husks for small-scale power generation in rice mills and other small factories in Cambodia has spread rapidly in the past decade and has a favourable investment payback period where the facility is off-grid. The technology is widely regarded as a sustainable, low-carbon power option. However, installed gasification technologies produce a black waste water which is frequently disposed of into the local environment without any treatment. An analysis was undertaken to identify and measure the key potential contaminants and compare concentrations in the water and sediment with regulatory thresholds established in Cambodia and within other jurisdictions. It was found that concentrations of organic contaminants such as phenols and benzene-type molecules (BETX) (water and sediment) and polycyclic aromatic hydrocarbons (PAHs) (sediment), as well as macro water quality indicators, were far higher than regulatory thresholds prescribe, posing threats to sensitive aquatic ecosystems into which such waste is introduced.

## List of Abbreviations

ARCS: The Assessment and Remediation of Contaminated Sediments program in the Great Lakes (North America)

BETX: benzene, ethylbenzene, toluene, xylene

BOD(5): biological oxygen demand (5 day incubation)

COD: chemical oxygen demand

DO: dissolved oxygen

EC: electrical conductivity

EIA: Environmental Impact Assessment

EMP: Environmental Management Plan

EU: European Union

FAO: Food and Agriculture Organisation

ILCC: Industrial Laboratory Centre Cambodia

kW: kilowatts

MPL: maximum permissible limit

NWSS: Northumberland Water Scientific Services Ltd.

OEM: Original Equipment Manufacturer

PAHs: polycyclic aromatic hydrocarbons

RDIC: Resource Development International – Cambodia

RHC: rice husk char

SDWPC: Sub-Decree on Water Pollution Control

SQUIRTS: Screening Quick Reference Tables (National Oceanographic and Atmospheric Administration (NOAA), USA)

TDS: total dissolved solids

TSS: total suspended solids

USEPA: United States Environmental Protection Agency

UV: ultra-violet

# 1. Introduction

In the past decade there has been a rapid expansion in the number of installed small-scale gasification units in Cambodia, providing power to rice mills and to ice-making and garment factories. The gasifiers use rice husk as the fuel and there are over 100 installed units in Cambodia operating in the range of 100 kW to 500 kW capacity. Rice husk gasifiers make economic sense where mills or factories are not connected to a national grid and/or where consumers pay market prices for electricity (i.e. absence of government subsidies). Such conditions apply in Cambodia (Shackley et al. 2012, 2012a) which accounts for the rapid diffusion of the technology in factories with small-scale motive power or electricity demand. The Original Equipment Manufacturer (OEM) is Ankur Scientific Pvt. Limited, a company based in Vadodara, Gujarat, India, but several ‘copy-cat’ firms have emerged in Cambodia over the past 5 years which are producing similar designs to Ankur’s but at lower cost, due to domestic manufacturers’ not having to pay import duties.

The older installed gasifiers - built and installed prior to 2010 - use water in two ways: to cool and scrub particles and tars out of the hot syngas which emits from the gasification unit (in Venturi scrubbers, the water being sprayed from above while the hot gas is introduced at the base and rises to meet the water); and to cool and remove the rice husk char (RHC) which is the solid waste or by-product of the gasification process. A dry-char discharge model has been available from the OEM from around 2009, which does not mix the waste water from the tar stripper with the char. The RHC is instead removed from the base of the reactor with a screw auger that deposits the RHC several meters from the reactor and allows it to be bagged-up for removal. The dry-char discharge design means that the RHC does not come into contact with potential contaminants that are present in the black waste water stream;

hence the RHC consists primarily of carbon, silica and ash. Likewise, the waste water does not come into contact with RHC particles, some of which become suspended in the water.

The waste water becomes black due to its contact with bio-oils and tars (in the scrubber) - and with char in the wet-discharge model - and is therefore known as 'black water'. The black water is sent by pipe to a settling pond or tank just outside the housing of the reactor. There are frequently 2 to 4 settling ponds constructed of concrete and lying in sequence and typically 1.2 to 1.5 meters deep and 3 - 4 meters long and wide. There is no consistent design, however, and the size, shape and number of settling ponds varies from site to site. The hot waste water cools in these ponds, moving from an entry-level pond to other ponds, and solid particles settle out and form a sediment or sludge. Sludges collect in the bottom of the settling pond arising from rice husk char (whole and fragments), condensed tars, ash and dust produced in the gasifier, other chemicals (metal oxides, salts), etc. These sludges need to be removed from the settling ponds periodically (monthly, after which it will have formed a 30cm deep layer - depending on the load factor of the gasifier and properties of the rice husk) to avoid excessive siltation and reduction of the effective volume of the cooling pond. It is normal practice to dry sludges in large piles and then to dispose of them in local fields or to add them to the rice husk char (RHC) piles. Addition of sludges directly to land, or through mixing with RHC, could introduce contaminants in sludge to soil and into the ecosystem and/or the food chain.

The black water is pumped from the final stage settling pond and cooled in a shower-type device before being pumped back into the Venturi scrubber and re-used for gas treatment. The system is supposed to be 'closed' in the sense that all the water is re-used. It is necessary to replace the water on a weekly to ten day basis due to the accumulation of contaminants

which reduces the efficacy of the water in scrubbing the syngas. Most commonly, there is a pond at the back of units into which these black waters are discharged during water replacement ('end disposal pond'). There is no further water treatment at this stage. In addition to the disposal of the waste water that is replaced by fresh water, leakage of black water from the settling tanks has frequently been observed at sites due to over-flow suggesting that the settling tanks are frequently under-sized. During the rainy season over-flow also occurs due to the lack of cover of the settling tanks and the intensive rainfall that occurs.

The end disposal pond is typically much larger and deeper than the settling ponds (e.g. 20 to 40 m long by 5 to 20 m wide). In most cases, existing ponds located nearby to the facility are employed, though sometimes ponds have been dug out for the purpose. Sludge accumulates in the end disposal ponds during replacement of the black water but due to their size removal of the sludge for the function of the pond as an end disposal route to continue is not usually required (and is not readily practicable with existing equipment). In some cases there is no end disposal pond but rather the excess waste water flows into a local stream or is simply emitted into boggy ground behind the facility.

The low-lying delta on which most gasification facilities are built is subject to flooding during the wet season when the water table rises to the surface. The delta land is naturally swampy and contains many ponds and interconnected streams and rivers. There is therefore a risk of spreading of contaminants, polluted and nutrient-rich waste water resulting in damage to ecosystems and eutrophication. Drinking water is accessed from wells below the water table while surface waters are widely used for washing, cleaning and, by children, for swimming and recreation. These freshwater aquatic systems are highly productive fisheries supplying a large percentage of the protein intake of the Cambodian population. As the FAO

Cambodia office states: “Fish is the main source of protein in people’s diet and marine fisheries and fresh water fishing in lakes and waterways, in particular the Tonle Sap and the Mekong, contribute substantially to incomes, jobs and food security” (quoted at: <http://coin.fao.org/cms/world/cambodia/CountryInformation/Countryinformation2.html>).

Complex aquatic ecosystems such as the Mekong and its tributaries are highly sensitive to industrial, agricultural and domestic waste water pollution (Guong & Hoa 2012, Sebesvari et al. 2012, Wilbers et al. 2014).

Small-scale rice husk gasification units have been widely advocated as a sustainable energy-generation option, since they make use of a free or low-cost agri-residue (rice husk) which is most often available at (or nearby) the site of the gasifier itself. International development aid programmes have endorsed expansion of the biomass gasification sector in Cambodia and similar countries (e.g. the EU’s SWITCH Energy to Waste programme, managed in Cambodia by the Dutch development organisation SNV). However, the environmental impacts of such units have previously not been investigated. As part of the Energy to Waste programme, SNV therefore commissioned research on the environmental impacts by the author (Gatti et al., 2013) and this paper uses the results thereof to ask the questions:

- what are the characteristics of black waste waters arising from gasification units?
- what are the potential environmental impacts from the release of black waste waters into the local environment?

This study is the first to examine the environmental contaminants associated with small to medium-sized rice husk gasifiers.

## 1. Methodology

A number of gasifiers were selected from which sampling of waste waters was to be undertaken. The selection of facilities was determined by the following considerations: a) the

practicality and logistics of visiting and taking and transporting samples; b) the limited budget available for laboratory analysis of the samples collected; c) inclusion of several different gasifier designs and models; d) inclusion of gasifiers from a range of major rice-producing and processing locations in Cambodia; and (e) inclusion of gasifiers which are known to be operated and maintained in an exemplary fashion as well as ones known to be operated and maintained in a sub-optimal way and a few reactors ‘in the middle’.

The sampling for the study was undertaken during the dry season (early January 2013) and the land surrounding the gasifier installations was dry to marshy. The sample that was selected is shown in Table 1. Three provinces were included: Kandal, Siem Reap and Battambang. These three provinces are reasonably representative of the major rice growing provinces of Cambodia, broadly reflect the growing conditions in Cambodia, including river-delta topography. Three gasifier manufacturers were included: 6 from the sector-leading OEM, with approximately 40 gasifiers installed in Cambodia; two from the leading alternative and predominant Cambodian equipment manufacturer; and one from another copy-cat manufacturer. The OEM gasifiers are manufactured in India and imported unlike the two copy-cat designs, which are manufactured in Cambodia. This increases the cost of the OEM machines ( $\geq \$90k$ ) due to import duties (compared with the cost of copy-cat gasifiers  $\geq \$40K$  and  $\geq \$20K$ ). Hence price is not necessarily indicative of quality. It was important to include a few alternative gasifier designs in the study in order to allow a comparison of the environmental performance of different designs, though with such a small sample, it is likely that the performance is as much related to specific operation and maintenance as it is to design.

Gasifier 4 provides power for a village-scale micro-grid project, a rare example of such a project in Cambodia. The installed gasifier includes a dry char discharge system and also a waste water treatment system developed by the OEM consisting of an alum coagulation unit



which removes the larger particles from the liquid. The waste water then passes through sand and charcoal filters and emits as a treated water. The waste water treatment system only handles approximately 15% of the waste water generated at the site, however. Sampling from site 4 allows a comparison to be made of the effectiveness of this waste water treatment system.

The list of environmental indicators selected for characterising the samples is shown in Table 2, drawing on established protocols (Baker et al. 1991, Quaghebeur et al. 2005, Nollet 2000). Water and sludge (sediment) samples were collected from the settling tanks or ponds, from the end disposal pond and from adjacent ponds and streams. Each situation and context was different and a decision had to be taken on sampling once site access had been granted by the site owner. Table 3 provides a consistent terminology for description of samples tested *in situ* and removed for further laboratory analysis. Waste water samples were extracted at approximately 5cm below the surface, while sludge samples were extracted from the edge of water bodies. A range of containers are used for collection as provided by the analytical laboratories for specific measurement variable, including one litre amber glass jars and bottles, plastic tubes (50ml) and glass amber vials (40ml). The containers were filled according to the instructions of the analytical laboratories.

*In situ* measurement of the pH, temperature, dissolved oxygen (DO) and electrical conductivity (EC) of the waste water in the settling ponds, disposal ponds, adjacent ponds and streams was undertaken at the nine sites where feasible. It was not always possible to access streams, disposal ponds or settling ponds due to their inaccessibility. A hand-held Hach multi-probe instrument (HQ40d) was used for *in situ* measurements. Biological oxygen demand (BOD<sub>5</sub>), chemical oxygen demand (COD), total dissolved solids (TDS), total suspended solids (TSS), several metals and ions and oil and grease content were measured by laboratories in Cambodia (Resource Development International Cambodia (RDI-C) and the

Industrial Laboratory Centre of Cambodia (ILCC)). BOC5 and COD have to be measured within 48 hours of collection and samples were kept in cold boxes on collection until delivery at RDI-C labs within this time window.

No laboratories in Cambodia could measure the full suite of metals and organic compounds, such as BETX, phenols, C<sub>10</sub>-C<sub>40</sub> molecules and PAHs. Samples were sent to the UK for testing at Northumberland Water Scientific Services Limited (NWSS). Due to difficulties in obtaining an export license to remove the samples from Cambodia, the samples were left standing for a period of approximately 10 days at the airport. The coolant would have ceased to have any cooling effect after 24 hours in sub-tropical temperatures. For this reason, NWSS determined that the samples were out of stability for organic molecules and the results for these chemical species are not, therefore, accredited. It is to be expected that the organic material should have undergone some decomposition while waiting at the airport – in particular the more volatile and labile organic matter. The measurement of BETX and phenols might, therefore, be an underestimate. PAHs - especially that within sediments – are known to be recalcitrant and the laboratory results are likely to be more reliable but their storage conditions do not meet the requirements of the laboratory for accreditation purposes. Due to a limited budget, it was not possible to measure more than one sample of each category. Therefore, no measure of variance can be provided. A decision had to be taken whether to allocate resources to undertake duplicate measurements at a smaller number of sites or whether to measure the waste from a larger number of sites without duplicate measurement. Since this is the first time the gasification facilities have been subject to environmental analysis, and given the scope of the study commissioned by the funding organisation, it was decided to survey more widely and without duplication. This limits the conclusions which can be drawn from the study, though the high readings for many environmental indicators and contaminants is strongly indicative.

## 2. Establishment of Thresholds for Environmental Pollutants

In order to evaluate the level of a potential pollutant, comparison was made with the maximum permissible limits (MPLs) for water discharge standards in Cambodia, known as the Sub-Decree on Water Pollution Control (SDWPC) enacted in 1999 by the Council of Ministers. The SDWPC provides two standards - one for water discharge into protected water bodies (lower MPLs) and the other for water discharge into non-protected water bodies and sewers (higher MPLs). We take exceedance of the higher MPL as indicating pollution, while exceedance of the lower MPL but not the higher MPL indicates a warning sign that pollution may be occurring. (For some indicators, such as Dissolved Oxygen, the reverse occurs since a higher number indicates less pollution and a lower number a higher pollution level). This is an approximate way of relating the concentrations of different contaminants to available environmental thresholds, though is an approximate indication of harm, not a precise measurement.

There are no MPLs for organic molecules in discharged waste water in Cambodian legislation. We have therefore used the threshold values provided by a well known reference data base for MPLs in water and sediments – the Screening Quick Reference Tables of the National Oceanographic and Atmospheric Administration (NOAA) in the USA – known as SQUIRTs (Buchman et al., 2008). SQUIRTs provides MPLs for both acute (short-term) and chronic (persisting) exposure. Acute impacts arise from one-off pollution episodes, whereas chronic impacts arise from continued introduction of the chemical species into the water body. The acute MPL is used to indicate pollution while if the pollutant concentration is lower than the acute MPL but above the chronic MPL, this indicates potential pollution.

Since no standards for pollutants in sediments were identified in Cambodia, SQUIRTs has been drawn upon to provide a range of potential MPLs. For some pollutants, SQUIRTs provides several different thresholds arising from different regulatory systems and / or from application of different risk assessment methodologies. For inorganics the ARCS values provided in SQUIRTs have been chosen wherever possible (developed by the US Environmental Protection Agency, report reference 905-R96-008). While for organics, the Dutch standards are presented – both intervention MPL and target MPL. The target MPL is what the Dutch government recommends be aimed for, while the intervention MPL is the value at which some ameliorative action is required. Where the concentration in the sample exceeds the ARCS value (inorganics) or the intervention value (organics), the chemical is regarded as a pollutant. For organic contaminants, where the concentration lies between the intervention and the target levels, the chemical is regarded as a potential pollutant.

## 4. Results

### 4.1. Visual Inspection

At all nine sites visited there is seepage of black waste water into the local environment. This typically occurs as a result of the settling ponds over-flowing. However, it also appears that a certain volume of water is discharged routinely and intentionally at most of the sites, in one case (where we were able to measure it) at a rate of a few litres per minute. The facility managers commented that black waste water is changed every one week to ten days, the water being disposed of to the surrounding local environment, usually a disposal pond at the back of, or close to, the facility. Such ponds appear to have been dug for this purpose though they may receive other waste streams (such as from a garment factory in one case). In several cases, the waste water was carried away by streams, sometimes into swampy marsh areas close to the facility.

Most gasifiers are located in low-lying areas where the water table is close to the surface, especially during the wet season, during which time many fields in the delta regions of the Tonle Sap Lake and River and of the Mekong and Tonle Basac rivers and their tributaries become marshy, swampy or flooded fields. Because of the very flat topography, waste water streams tend to flow into (and contribute towards) marshy areas surrounding the facility.

Settling ponds contained hot to warm water which was brownish black in colour and had a large frothy 'scum' on its surface. The disposal ponds contained a blackish water with black banks and sediment. There was an absence of visible life forms in the ponds, either animal or plant. By contrast, several nearby ponds not receiving any visible waste contained water with good clarity, supporting vigorous growth of water lilies on the surface and plenty of insect and animal life (notably frogs) on the surface and within the water itself.

#### **4.2. Field Measurements of pH, Electrical Conductivity and Dissolved Oxygen**

In the large majority of cases the pH of the settling and disposal streams and ponds is neutral to somewhat alkaline, but well within the acceptable range. Electrical conductivity (EC) measures the presence of ions that carry a negative charge (e.g. chloride, nitrate, sulphate, and phosphate) as well as positively charged metal ions. The field measurements of EC in the waste water settling ponds and in the final disposal ponds are very high, indicating high levels of water pollution (Figure 1). Industrial waste waters can have an EC of around 10 millisiemens per cm (mS/cm).

Many of the settling and waste water disposal ponds exhibited an EC of 2 to 7 mS/cm.

Where we were able to measure baseline levels in ponds near to the gasifiers that were not receiving waste water, we found much lower EC values. At site 4, for example, the pond with no gasifier waste water input used as a baseline had an EC that was 30 times lower than the settling pond and 60 times lower than the disposal pond. The EC for settling pond water was

above the MPL for sites 1, 2, 3, 4 and 5 and also for the discharge stream water at sites 5, 6, 7 and 8 and for the disposal pond water at sites 4 and 9. However, the EC was below the MPL for the disposal pond water at sites 1 and 8.

Dissolved oxygen (DO) measures the quantity of oxygen in the water column. A lower DO indicates a greater demand for oxygen within the water body. High demand for oxygen in water bodies tends to indicate an over-abundance of algae, bacteria and / or cyanobacteria. Such over-abundance is usually associated with the introduction of too many nutrients such as nitrates and phosphates into the water column, as N and P are typically limiting factors for algal growth in water. Hence, high levels of DO typically indicate a less polluted water system while low levels indicate presence of pollutants. The DO measurements in the ponds not in receipt of gasifier black waste water tended to be in the order of 4 to 7 mg per litre, whereas the settling and disposal ponds exhibited very low DO levels, around 0.15 to 0.4 mg per litre, indicative of high levels of pollution (Figure 1). The DO levels were too low compared to MPLs for sites 1 (settling pond and disposal pond), site 2 (settling pond water), site 3 (settling pond water), site 4 (disposal pond water), site 8 (disposal pond water) and site 9 (disposal stream water and disposal pond water).

#### **4.3. Laboratory Measurements of BOD<sub>5</sub>, COD, Nitrates, Phosphates and Chlorides**

BOD<sub>5</sub> and COD were measured on fresh samples in the laboratory delivered within 48 hours of collection. The large majority of cases showed very high BOD<sub>5</sub> and COD levels (Figures 2 & 3) – an order of magnitude greater than the regulatory maximum permissible limits (MPLs) in Cambodia in many instances; and two orders of magnitude greater than the level in ponds not receiving waste water in the vicinity of the gasifiers. For example, at site 4 the BOD<sub>5</sub> in the adjacent pond not receiving gasifier waste water was 3 mg per litre, while it was 320 mg

per litre in the disposal pond water. The regulatory limit is 80 mg/l for a public water body and sewer. The equivalent COD values were 37 mg/l (baseline pond receiving no gasifier black water waste) and 2840 mg/l (disposal pond) with the regulatory limit of 100 mg/l (Figures 2 & 3).

BOD5 and COD levels were beyond the discharge standard level at site 4 – both settling pond and disposal pond - but not at the waste water treatment facility. This suggests that the waste water treatment plant is effective for the portion of waste water that it treats (15% of total) but that the remaining 85% that is not treated results in organic pollution in the disposal pond. BOD5 and COD are exceeded (relative to the regulatory threshold) in the disposal stream water at site 7 and also in the disposal stream water and disposal pond water at site 9. All the waste water samples tested for BOD5 and COD exceeded the MPL with the exception of the treated waste water at site 4. The pond water at site 4, which was receiving no gasifier waste and used as a baseline, had a very low BOD5 and COD.

Measurements of nitrates and phosphates in water samples confirm moderately high levels that are sometimes above the regulatory maximum permissible limits (MPLs) (Figure 4). The concentration of nitrates in the water emitting from the waste water treatment system at site 4 is nearly four times greater than the MPL for nitrates in discharge water in Cambodia. The total suspended solids (TSS) and the total dissolved solids (TDS) are higher than the MPL in the case of most waste water samples tested (Figure 5).

#### **4.4. Laboratory Measurements of Metals in Water and Sludge Samples**

Metal levels in water samples tested are largely within acceptable levels for waste water discharge in Cambodia, with the exception of iron and copper in a few instances (Figure 4). Note that if total metals in the sample are measured (not just the dissolved fraction) then other elements begin to look potentially too high, including arsenic, mercury and zinc. In the

majority of cases, however, metal pollution does not appear to be a major problem in waste water samples arising from the gasifiers. The sludge samples tested tend to show levels of several metals that are beyond the MPL, presumably due to accumulation, e.g. for zinc (sites 1, 4, 10), chromium (site 4), nickel (sites 4, 10), copper (site 4), iron (site 8), lead (site 10) and manganese (site 10) (Figure 4 and 6).

#### **4.5. Laboratory Measurements of Organic Compounds in Water and Sludge / Sediment Samples**

There are three main groups of organic substances that were identified as potential contaminants – BETX (benzene, ethylbenzene, meta + para xylene, orthoxylene and toluene), phenols and PAHs (polycyclic aromatic hydrocarbons). At site 1, there are very high levels of BETX in the disposal and settling pond sludge (Figure 10). There are very high levels of PAHs in the disposal pond sediment and high levels of cresol in the settling pond water (560 times greater than the MPL) (Figures 7 & 8). At site 3, BETX levels in settling pond water are high, as also are PAH levels in the settling pond sludge, though much less than at site 1 (Figure 8 & 10). Cresols levels in sludge from the first settling pond at site 3 were below the MPL. At site 4, BETX levels are reasonably high for settling pond water, settling pond sludge and disposal pond water, though less than at site 1. PAH levels are high for settling pond water sludge at site 4. Levels of PAHs are also beyond the MPL in the sludge from the waste water treatment system at site 4, similar to the levels in the disposal pond sediment, but 5% to 30% of the levels in the normal settling pond sludge (i.e. without the water treatment system) (Figure 8 & 9). Hence, the waste water treatment system is removing 70 to 95% of the PAHs in the sludge compared to the untreated settling tank sludge, but the levels remaining are still far above the MPL. For example, the total PAHs for settling pond sludge are between 10,000 and 68,000 mg/kg, while for the sludge from the waste water treatment pond the concentration is 3,300 mg/kg. However, the Dutch target MPL is 1 mg/kg while the



intervention MPL is 40 mg/kg. The PAH levels in the disposal pond sludge at site 4 are slightly lower than those in the waste water treatment facility sludge, possibly due to more effective microbial decomposition; however, the total is 2,600 mg/kg, still much higher than the MPL.

Cresols levels in disposal pond water at site 4 were 135 times higher than the MPL, while phenol is nine times greater than the MPL (Figure 7). Meanwhile, the cresols in settling pond sludge at site 4 are three times the MPL and 2.3 times for phenol (Figure 7). The values of cresols and phenol in waste water and sludge from the waste water treatment plant at site 4 were much lower than in non-treated water and associated sediments (below the target threshold for water and between the target and intervention MPL for sediment). The PAHs in the sludge from the waste water treatment plant were, however, above the MPL. This demonstrates that the water treatment process operated effectively for cresols and phenols but not as effectively for PAHs. Concentrations of cresols and phenol in sludge from the alum coagulation unit, the part of the water treatment system which removes particles, were very high (25 times the intervention MPL for both). Careful and safe disposal of this solid waste is, therefore, necessary.

At sites 5 and 6, waste water from the settling ponds and disposal stream water exceed the MPLs for several of the BETX species (Figure 10). The sludge from stream discharge at site 5 exceeds the MPL for benzene and for a number of PAHs though concentrations are a lot less than at other sites such as 1 and 4. The concentration of cresols in the sludge from the disposal stream at site 6 is below the MPL. Settling pond sludge at site 7 exceeds MPLs for a number of PAHs but with much lower levels than at sites 1 and 4. Disposal pond sludge at site 9 is moderately high in BETX and exceeds the MPLs for several PAHs. The water from the disposal pond has a high concentration of cresols (260 times MPL) and phenol (28 times MPL) (Figure 7).

Figure 8 and 9 plots data on the total PAHs in water and sludge samples from different sites and reactors, while Figure 10 presents data for BETX. It can be seen that gasifiers (1) and (4) have far higher levels of BETX and PAHs than the other gasifiers. Removing the highest concentrations allows a comparison to be made of the lower concentrations of PAHs from the other gasifiers, as in Figure 9. It is likely that the levels of PAHs depend upon the operational history and on-going operation of the gasifier – e.g. the length of time it has been operating, the load factor and how the gasifier is operated, local environmental conditions such as dispersal of pollutants from disposal ponds, etc. Site (4) is operating 24 hours a day for 7 days a week so creating a much larger amount of waste water and sludge than other gasifiers which have a much lower (seasonal) load factor. Gasifiers that are not running as frequently produce less waste and there is more time for degradation and oxidation of organic chemicals.

PAHs are strongly hydrophobic. The log Kow (the octanol-water partition coefficient) is used to measure the hydrophobicity of a chemical and values  $>2.5$  are considered to indicate hydrophobicity. PAH log Kow can be as high as 5 (e.g. phenanthrene). Due to hydrophobicity, PAHs are readily attracted and attached to particles in the water column which drift down the water column to form sediment under gravity. PAHs within sediment, especially under anaerobic conditions, are resistant to decomposition by microorganisms and are removed from the effect of UV light. This explains why PAH concentrations in sediment and sludge from settling and disposal ponds are high to very high, while concentrations in the waste water are generally low. The log Kow value for phenol and cresols are in the range of 1.5 to 2, so hydrophilic rather than hydrophobic and therefore have a stronger tendency to remain within the water column. On the other hand, it is known that biochar with functional groups such as  $-NH_2$  and  $-C=O$  will sorb phenol, including rice husk biochar (Liu et al., 2011). Cresols have been shown to sorb well onto manure based biochars due to the basic

nature of the biochar functional groups (Fitzgerald et al., 2014). While rice husk biochar from the gasifier is unlikely to contain as many functional groups as manure biochar, due to the high temperature of gasification, it is still likely that sorption of phenol and cresols onto rice husk biochar particles with the waste water column or within the sediment would occur to some extent.

## 5. Discussion

The analysis of data has demonstrated that the black waste waters produced by the Venturi scrubbing units, and, in the older designs, by the rice husk char removal stage, are heavily polluted on a number of counts: they have very high Biological and Chemical Oxygen Demand (BOD5/COD), correspondingly low levels of dissolved oxygen (DO), a high electrical conductivity (EC) and a large amount of Total Suspended and Dissolved Solids (TSS, TDS). All these variables indicate water with a high amount of undigested organic matter and associated nutrients. Microbial growth is stimulated by the availability of nutrients such as organic and mineral P and N as well as carbon, removing oxygen from the water body and producing eutrophication.

Furthermore, the water contains high levels of organic contaminants, especially phenol, cresols, some PAHs and, in a few cases, benzene-type molecules (BETX). BETX, phenols and PAHs are frequently toxic to organisms above specified concentrations (Ball and Truskewycz 2013, Gauthier et al. 2014, Harris et al. 2013, Manzetti 2013, Minh et al. 2004, Ram et al. 1990). Benzene is a known human carcinogen (Group A), while ethyl-benzene, toluene and xylene are not classifiable as to human carcinogenicity according to the US Environmental Protection Agency (Group D) though acute and chronic health impacts on humans and experimental animals are well documented ([www.epa.gov](http://www.epa.gov)). Phenol is not classifiable as to human carcinogenicity according to the USEPA (Group D) though acute

and chronic health impacts occur in humans and in animal studies (ibid.). Cresol is a possible human carcinogen according to the USEPA (Group C) with known acute health impacts on humans and chronic impacts observed in animal studies (ibid.). Some PAHs are probable human carcinogens (Group B) including benzo[a]pyrene, benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, dibenzo[a,h]anthracene and indeno[1,2,3-cd]pyrene. PAHs also have known acute and chronic human health effects (ibid.). Hence, the fact that concentrations of these chemicals in gasifier waste waters and sediments are frequently much higher than the MPL is a cause for concern.

These chemicals are present at such high concentrations that they will pose a direct hazard to plants, fish, amphibians, insects and higher life forms. Specialised microorganisms are able to break down the above chemicals and a strong selective pressure will favour their proliferation, further reducing the dissolved oxygen. For these reasons, the disposal ponds will become largely dead zones with respect to insects, plants, amphibians and fish. PAHs, being strongly hydrophobic, will attach to particles which form sediment and be removed from the water column. However, such PAHs are unlikely to be accessible to degradation by the action of abiotic (e.g. UV) and/or biotic (microbial) factors.

While PAHs within sediment are largely inaccessible, and consequently not a hazard to higher life forms, their very slow decomposition rate means that the sediments and sludges remain a health hazard. The sludge from the settling ponds is removed daily and dumped in piles on land next to the facility or on adjacent land. Such action increases the bio-availability of PAHs and could increase exposure to animals, including humans. Sediment collecting in disposal ponds is not generally removed, but it may accumulate to such an extent that either it has to be dredged or a new end disposal pond is required. Either way, the sediment remains a long-term health hazard and limits future use of the pond and land on to which sediment is piled. For example, plants growing on land upon which sludges and

sediments have been deposited may absorb heavy metals and recalcitrant organic molecules, so posing a risk to humans through direct ingestion of crops or of animal products ingesting the plants.

Sludge from the gasifier settling ponds is sometimes spread onto the surface of grazing land, with some direct ingestion by animals. This sludge can contain high concentrations of manganese (2688 mg/kg) as well as of PAHs (e.g. 1214 mg/kg for naphthalene). The risk to animals and humans of ingesting potentially toxic chemicals is unacceptably high and the recommendation is not to use this material for spreading onto soil where animals are grazing. There is a risk of long-term liability associated with the sites due to persistence of heavy metals and some organic pollutants. While the present legal system in Cambodia would be unlikely to pursue such claims, future improvements to the legal system are likely and if operators knowingly expose others to risk they could be held liable in the future.

To summarise, the data that has been assembled indicates that the black waste water streams cause serious localized pollution of end disposal ponds and of streams into which the black water flows. Some of this pollution is persistent, as in accumulation of heavy metals in the water body (copper and iron), while zinc, chromium, manganese, copper, nickel and lead accumulate in some of the sediments tested. The high Electrical Conductivity measurements are indicative of the presence of negatively and positively charged ions and, where measured, moderate to high levels of nitrate, chloride and phosphate were discovered.

Of even more concern is the introduction of large quantities of organic molecules into the water bodies. The very high Biological and Chemical Oxygen Demand (where measured) indicates the high loading of ponds and streams with a complex mixture of organic compounds. This high loading and associated high BOD and COD is reflected by low measured DO levels and effectively kills-off non-microbial forms of life in ponds and streams

such as fish, frogs, plants and macro-invertebrates (insects, spiders, crustaceans) which are unable to survive in such low oxygen water bodies also containing potential toxic compounds.

Very high levels of single benzene-ring type molecules (phenols and cresols and, in a few instances, BETX) were discovered in waste water and sediment samples tested. Polycyclic aromatic hydrocarbons (PAHs) (composed of two, three, four and five-benzene ring molecules) were measured at very high levels in most of the sediment samples and, at lower concentrations, in the waste water samples. Somewhat lower PAH levels were measured in sediment from the disposal pond at site 9, receiving waste water from the longest running gasifier in Cambodia. It is possible that presence of phenols, cresols, BETX and PAHs over a time period of years have provided a strong selective pressure for microorganisms that are able to breakdown such molecules and use them as a source of carbon and energy, hence there is a higher turn-over of the organic contaminants. Laboratory incubation studies would be required to test this hypothesis. If demonstrated, such microbial cultures from the disposal pond at site 9 might be used to help breakdown of persistent organic pollutants at existing sites.

Whether the organic and inorganic pollution can disperse from the disposal ponds and marshy areas laterally or vertically through the water table is not known and was not tested for in this study. A more detailed hydrological analysis and survey would be required to determine whether this is a problem or not but there seems at least a possibility that dispersion could happen for more mobile pollutants.

Site 4 is the only gasifier in Cambodia which has a waste water treatment system. This system works well and the resulting water has a high DO and low EC and no significant level of pollutants in the waste water. However, the sludge collected from the waste water

treatment system still contains very high levels of PAHs. The waste water treatment system at site 4 only has the capacity to treat 15% of the waste water arisings from the gasifier. The other 85% remains untreated and flows into the disposal pond. The water quality in the final disposal pond is very poor and no better than that in other waste water disposal ponds. Clearly, the waste water treatment system would need to be scaled-up to treat all of the waste water. The capital and operational costs of scaling-up the waste water management system to cope with 100% of the waste water are prohibitive.

A key limitation of this study is that only one sample in each category and variable type was measured due to resource constraints. Without a measure of variance, it is not possible to provide a mean value and standard error for each variable. Furthermore, the sampling was constrained by the resource available for laboratory analysis and took place only in the dry season when the water table is much lower than during the wet season. More representative sampling would include taking samples throughout the year and under different rainfall and water table conditions. In addition, the load factor of the mills, hence of the gasifiers, varies due to fluctuating demand throughout the year and this will greatly influence the volume of black water generated per day and week. This is a further factor to take into account in a sampling strategy aimed at improving representativeness. All the gasifiers sampled from are located in the flood plain of the Mekong River or Tonle Sap Lake / River. Since the vast majority of rice mills (and factories using gasifiers) are based on the flat delta land, this is representative of the topographical conditions in Cambodia.

## 6. Implications

None of the sites visited had an Environmental Management Plan (EMP) in place. While an EMP is not required in Cambodian law at the present time, development of such would be a useful way for operators and owners to meet their obligations under the laws which do cover the operation of biomass gasifiers. This includes the likely requirement in Cambodia in the next few years for a more detailed Environmental Impact Assessment (EIA). The legal framework is largely already in place, but requires more detailed sub-decrees and guidance and, most importantly, enforcement by regulatory agencies. The key elements of an EMP for the gasification facilities are described below.

1. **Waste Water Management.** Further development of gasifiers without appropriate waste water treatment systems that manage a large majority of the waste water arisings risks polluting the environment local to the facilities. The long-term effect of such pollution is unknown but could posit a long-term threat to human health and local ecosystems, reduce the ability to utilize land in the future for food production and could pollute human drinking water sources. The waste water treatment system designed by the OEM works well but, if it only treats 15% of the waste water (as at site 4), it does little to reduce environmental pollution to the local environment. Therefore, the waste water treatment system has to be large enough to cope with 100% of the waste water arisings. This might require the use of several waste water treatment systems ‘in parallel’, where additional units can be brought online as load factor increases.
2. The sludge (sediment) from the bottom of the settling ponds, disposal ponds and streams contains high levels of toxicants and should be managed as a special waste and disposed of appropriately. Drying settling pond sludge and its combustion with abatement of the emissions, use as an ingredient in building materials or else disposal to a waste handling



facility (e.g. a licensed landfill site), is strongly recommended. The sludge should not be disposed of in the local environment, nor should sludge be added to the piles of rice husk char, since this risks contaminating the rice husk biochar which can be utilised as a soil amendment (Shackley et al., 2012 and 2012a).

3. The various sludges produced by the waste water treatment system will need to be handled as special wastes and disposed of appropriately, e.g. dried and used in building material, incinerated or land-filled, etc.
4. Dry char discharge systems for the rice husk char are desirable as they reduce the waste water arisings. Dry char discharge is now installed on newer OEM gasifier units and a number are already operating in Cambodia (e.g. site 4 and 8).
5. The OEM is developing a 'dry' gas treatment system. The intention is that this will remove the generation of black waste water arisings completely. As yet there is insufficient independent evidence on the efficacy of dry gas treatment systems when rice husk is used as the fuel. If robust evidence of the efficacy of dry gas treatment is available, use of the equipment would help to avoid many of the environmental pollution problems discovered in this analysis. The wastes such as BETX, heavy metals and PAHs will still be present or generated, however, so appropriate disposal by gaseous combustion or safe disposal of the solid waste stream from the gas treatment unit will still be essential.
6. The Rice Husk Char (RHC) needs to be kept separate from the waste water streams to avoid sorption of metals or organic contaminants into the char, thereby introducing the possibility of adding toxicants to soil if RHC is added to land.

## Acknowledgements

The research was funded by the EU SWITCH Energy-to-Waste programme, managed by SNV and Nexus (EuropeAid/130830/C/ACT/CAI). The author thanks the following for their assistance: Eleonara Gatti, Sam Bryan, Benjamin Lamberet, Bona Sam, Putheary Kuy, Sar

Samnang, Anthony Wilson, Tony Knowles and the facility managers and owners who gave permission to sample materials on site and to remove samples for laboratory analysis. The author is very grateful to the two anonymous peer-reviewers, whose comments have much improved the paper.

## References

- Baker, R. (Ed.) (1991) *Organic Substances and Sediments in Water, Volume 2: Processes and Analytical*, Lewis Publishers Inc. Michigan, USA.
- Ball, A. and A. Truskewycz (2013) 'Polycyclic aromatic hydrocarbon exposure: an ecological impact ambiguity', *Environmental Science and Pollution Research*, Vol. 20, No. 7, pp. 4311-4326.
- Buchman, M. F. (2008) *NOAA Screening Quick Reference Tables, NOAA OR&R Report 08-1*. Office of Response and Restoration Division, US Government, Seattle, WA.
- Cenci, R. and Martin, J. (2004) 'Concentration and fate of trace metals in Mekong River Delta', *Science of the Total Environment*, Vol. 332, No.1-3, pp. 167-182.
- Fitzgerald, S., Kolar, P., Classen, J., Boyette M. and Das L. (2014) 'Swine manure char as an adsorbent for mitigation of p-cresol', *Environmental Progress and Sustainable Energy*, DOI: 10.1002/ep.11972.
- Gatti, E., Bryan, S., Say, C., Lamberet, B. and Shackley, S. (2013), *Services for an Emissions Reducton Project Baseline, Feasibility and Environmental Study*, Final Report, Nexus for EU SWITCH-Asia funded project: Waste to Energy (WtE) for the Rice Milling Sector in Cambodia, EuropeAid/130830/C/ACT/CAI.
- Gauthier, P., Norwood, W., Prepas, E. et al. (2014) 'Metal-PAH mixtures in the aquatic environment: A review of co-toxic mechanisms leading to more-than-additive outcomes', *Aquatic Toxicology*, Vol. 154, pp. 253-269.
- Guong, V.T. and Hoa, N.M. (2012), 'Aquaculture and agricultural production in the Mekong Delta and its effects on nutrient pollution of soil and water', in Renaud, F. and Kuenzer, C. (Eds.), *Mekong Delta System: Interdisciplinary Analyses of a River Delta*, Springer Environmental Science and Engineering, Berlin, Germany, pp. 363-393.
- Harris, K., Banks, L., Mantey, J. et al. (2013) 'Bioaccessibility of polycyclic aromatic hydrocarbons: relevance to toxicity and carcinogenesis', *Expert Opinion on Drug Metabolism and Toxicology*, Vol. 9 No.11, pp. 1465-1480.
- Liu, W.-J., Zeng, F.-X., Jiang, H. and Zhang, X.-S. (2011), 'Preparation of high adsorption capacity bio-chars from waste biomass', *Bioresource Technology*, Vol. 102, pp. 8247-8252.
- Manzetti, S. (2013), 'Polycyclic aromatic hydrocarbons in the environment: Environmental fate and transformation', *Polycyclic aromatic compounds*, Vol. 33, No. 4, pp. 311-330.
- Minh, N.H., Tu, B. and Kajiwar, N. et al. (2004), 'Pollution sources and occurrences of selected persistent organic pollutants (POPs) in sediments of the Mekong River delta, South Vietnam', *Chemosphere* Vol. 67, No. 9, pp. 1794-1801.

Nollet, L.M. (Ed.), (2000) *Handbook of Water Analysis*, Marcel Dekker Inc. , New York, USA.

Quaghebeur, D., Temmerman I. and Angeletti G. (eds.) (2005) *Organic Contaminants in Waste Water, Sludge and Sediment: Occurrence, Fate and Disposal*, Elsevier Applied Science, Dordrecht, Netherlands.

Ram, N., Christman, R. and Cantor, K. (1990). *Significance and Treatment of Volatile Organic Compounds in Water Supplies*, Lewis Publishers, Michigan, USA.

Sebesvari, Z., Huong, T.T.L., Pham V.T et al. (2012). 'Agriculture and water quality in the Vietnamese Mekong Delta' in Renaud, F. and Kuenzer, C. (Eds.), *Mekong Delta System: Interdisciplinary Analyses of a River Delta*, Springer Environmental Science and Engineering, Berlin, Germany.

Shackley, S., Carter, S., Knowles, T., Middelink, E., Haefele, S., Sohi, S., Cross A. and Haszeldine S. (2012) 'Sustainable gasification-biochar systems? A case study of rice-husk gasification in Cambodia Part I: Context, chemical properties, environmental and health and safety issues', *Energy Policy*, Vol. 42, pp. 49-58.

Shackley, S., Carter, S., Knowles, T., Middelink, E., Haefele, S., Sohi, S., Cross A. and Haszeldine S. (2012a) 'Sustainable gasification-biochar systems? A case-study of rice-husk gasification in Cambodia, Part II: Field trial results, carbon abatement, economic assessment and conclusions', *Energy Policy*, Vol. 41, pp. 618-623.

Wilbers, G.-J., Becker, M., Nga, L., Sebesvari Z. and Renaud F. (2014) 'Spatial and temporal variability of surface water pollution in the Mekong Delta, Vietnam', *Science of the Total Environment*, Vol. 485, pp. 653-665.

Tables and Figures to Accompany MS: Characterisation of Waste Water from Biomass Gasification Equipment: A Case-Study from Cambodia

Site Number	Province	Gasifier Manufacturer & Model	Samples tested <sup>2</sup>			Sampling Strategy
			W	S	Σ	
1	Kandal	Ankur FBG200	3	2	5	1 <sup>st</sup> and 6 <sup>th</sup> settling pond sampled (out of six). Disposal pond
2	Kandal	Ankur Combo 350 kW	1		1	1 <sup>st</sup> settling pond (out of two)
3	Kandal	Seng Kuch	2	1	3	1 <sup>st</sup> and 2 <sup>nd</sup> settling pond (out of two)
4	Siem Reap	Ankur <sup>1</sup>	4	2	6	1 <sup>st</sup> settling pond (out of three). Waste water treatment unit. Disposal pond. Pond with no input of gasifier waste water
5	Siem Reap	Chanrorn	3	1	4	1 <sup>st</sup> and 2 <sup>nd</sup> settling pond (out of two)
6	Siem Reap	Ankur FBG150	2	1	3	Disposal stream.
7	Battambang	Chanrorn	1	1	2	2 <sup>nd</sup> settling pond (out of two). Disposal stream
8	Battambang	Ankur	1	1	2	Disposal stream
9	Battambang	Ankur FBG200	4		4	Disposal stream. Two ponds with no gasifier waste water input. Disposal pond
10	Existing sample taken at site 6 in 2010	Ankur FBG150	2	1	3	Early opportunistic sampling attached to another project
Total			23	10	33	

Table 1: List of gasifiers sampled

(1) Dry char discharge and with waste water treatment system installed on 15% of waste water arisings

(2) W = waste water; S = sludge / sediment

Parameter (in alphabetical order under sub-headings)	Units	Method Used	Purpose of Measurement
			<b>Aggregate Water Indicators</b>
BOD5	DO $\text{mg l}^{-1}$	BOD5 (in-house)	The BOD5 refers to the amount of oxygen in milligrams consumed per litre of the sample over five days incubation at 20°C. It is one of the standard tests used to characterize effluent quality and measures organic pollution in surface waters” (Morris & Therivel, 2001).
COD	DO $\text{mg l}^{-1}$	Digestion, colorimetric spectrophotometry (in-house)	COD measures all organic matter than can be chemically oxidized, not just the biologically active organic matter. It is therefore more wide-ranging than BOD5.
Dissolved oxygen	DO $\text{mg l}^{-1}$	Meter	Dissolved oxygen (DO) measures the quantity of oxygen in the water column.
Electrical conductivity	$\text{mscm}^{-1}$	Meter	Electrical conductivity (EC) measures the presence of ions that carry a negative charge (e.g. chloride, nitrate, sulfate, and phosphate) as well as positively charged metal ions.
pH	pH units	Meter	A measure of the acidity or alkalinity of a liquid or of a solid that is in solution.
Temperature	°C	Meter	
Total dissolved solids (TDS)	$\text{mg l}^{-1}$	Meter AOAC 973.40	A measure of the mass of all organic and inorganic substances contained in a liquid in molecular, ionized or micro-granular suspended form, which are small enough to pass through a two micrometer filter.
Total suspended solids (TSS)	$\text{mg l}^{-1}$	Filtration AOAC 920.193	A measure of the mass of solid particles which are suspended in the water and removed when the liquid is passed through a two micrometer filter.
			<b>Inorganic Elements and Ions</b>
Aluminium	$\text{mg l}^{-1}$ ( $\text{mg kg}^{-1}$ )		An element which can be toxic at high concentrations
Antimony	$\text{mg l}^{-1}$		An element which can be toxic at high concentrations
Arsenic	$\text{mg l}^{-1}$ ( $\text{mg kg}^{-1}$ )	Atomic fluorescence spectrophotometer; ICP-MS	An element which can be toxic at high concentrations
Barium	$\text{mg l}^{-1}$		An element which can be toxic at high concentrations

Beryllium	mg l <sup>-1</sup>		An element which can be toxic at high concentrations
Boron	mg l <sup>-1</sup> (mg kg <sup>-1</sup> )	ICP-OES	An element which can be toxic at high concentrations
Cadmium	mg l <sup>-1</sup> (mg kg <sup>-1</sup> )	ICP-MS	An element which can be toxic at high concentrations
Calcium	mg l <sup>-1</sup>		An element
Chloride	mg l <sup>-1</sup>	Ion chromatography;	An ion which can be toxic at high concentrations
Chromium	mg l <sup>-1</sup> (mg kg <sup>-1</sup> )	AOAC 974.27; ICP-MS	An element which can be toxic at high concentrations
Cobalt	mg l <sup>-1</sup> (mg kg <sup>-1</sup> )	ICP-MS	An element which can be toxic at high concentrations
Copper	mg l <sup>-1</sup> (mg kg <sup>-1</sup> )	AOAC 9; ICP-MS 74.27	An element which can be toxic at high concentrations
Fluoride	mg l <sup>-1</sup>	Ion chromatography	An ion which can be toxic at high concentrations
Iron	mg l <sup>-1</sup>	AOAC 974.27	An element which can be toxic under certain conditions
Lead	mg l <sup>-1</sup>	AOAC 974.27; ICP-MS	An element which can be toxic at high concentrations
Magnesium			An element
Manganese	mg l <sup>-1</sup>	Colorimetric spectrophotometry; and AOAC 974.27	An element which can be toxic at high concentrations
Mercury	mg l <sup>-1</sup> (mg kg <sup>-1</sup> )	Atomic fluorescence spectrophotometer	An element which can be toxic at high concentrations
Molybdenum	mg l <sup>-1</sup> (mg kg <sup>-1</sup> )	ICP-MS	An element which can be toxic at high concentrations
Nickel	mg l <sup>-1</sup> (mg kg <sup>-1</sup> )	ICP-MS	An element which can be toxic at high concentrations
Nitrate	mg l <sup>-1</sup> as NO <sub>3</sub> <sup>-</sup>	Ion chromatography	An ion which is a mineral form of N and can cause eutrophication
Potassium	mg l <sup>-1</sup>		An element
Phosphate	mg l <sup>-1</sup> as PO <sub>4</sub> <sup>3-</sup>	Ion chromatography	An ion which is a mineral form of P and can cause eutrophication
Selenium	mg l <sup>-1</sup> (mg kg <sup>-1</sup> )	ICP-MS	An element which can be toxic at high concentrations
Silicon			An element
Sodium	mg l <sup>-1</sup> (mg kg <sup>-1</sup> )	Ion chromatography; ICP-OES	An element which can be toxic at high concentrations
Strontium	mg l <sup>-1</sup>		An element which can be toxic at high concentrations
Titanium	mg l <sup>-1</sup>		An element which can be toxic at high concentrations
Vanadium	mg l <sup>-1</sup>		An element
Zinc	mg l <sup>-1</sup> (mg kg <sup>-1</sup> )	ICP-MS	An element which can be toxic at high concentrations
			Organic Compounds
Benzene	mg kg <sup>-1</sup> (mg l <sup>-1</sup> )	Purge and trap GCMS	volatile aromatic single carbon-ring molecules which can be toxic
Ethyl benzene	mg kg <sup>-1</sup> (mg l <sup>-1</sup> )		
Meta- and para-xylene	mg kg <sup>-1</sup> (mg l <sup>-1</sup> )		
Ortho-xylene	mg kg <sup>-1</sup> (mg l <sup>-1</sup> )		
Toluene	mg kg <sup>-1</sup> (mg l <sup>-1</sup> )		
Total petroleum hydrocarbons (C10 to C40)	mg kg <sup>-1</sup> (mg l <sup>-1</sup> )		GC-FID
Oil & Grease	mg l <sup>-1</sup> (mg l <sup>-1</sup> )	APHA 5520-B	Oil-residues which can be persistent organic pollutants

Cresols	mgkg <sup>-1</sup> (mgl <sup>-1</sup> )	Methanol/water extraction followed by liquid chromatography and electrochemical detection (National Grid Standard, Environmental Assessment Guidance, Version 3, 2003).	Potentially toxic molecules
Ethylphenol and dimethylphenol	mgkg <sup>-1</sup> (mgl <sup>-1</sup> )		
Isopropylphenol	mgkg <sup>-1</sup> (mgl <sup>-1</sup> )		
Naphthols	mgkg <sup>-1</sup> (mgl <sup>-1</sup> )		
Trimethylphenol	mgkg <sup>-1</sup> (mgl <sup>-1</sup> )		
Total phenols	mgkg <sup>-1</sup> (mgl <sup>-1</sup> )		
Polycyclic Aromatic Hydrocarbons (PAHs)	mgkg <sup>-1</sup> (mgl <sup>-1</sup> )	Extraction with Dichloromethane (DCM) followed by GCMS	Potentially toxic and (in some cases carcinogenic) molecules
The sixteen individual PAHs regulated by USEPA are listed below plus two naphthalene-related compounds: Acenaphthene, Acenaphthylene, Anthracene, Benzo(a)anthracene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Benzo(a)pyrene, Benzo(g,h,i)perylene, Chrysene, Dibenzo(a,h)anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-cd)pyrene, 1-Methylnaphthalene, 2-Methylnaphthalene, Naphthalene, Phenanthrene and Pyrene.			

**Table 2: List of Measured Elements and Molecules, indicating method and purpose**

Legend: AOAC = Association of Official Agricultural Chemists; DCM = dichloromethane; GCMS = gas chromatography mass spectroscopy; ICP-MS = inductively coupled plasma mass spectroscopy; ICP-OES = inductively coupled plasma atomic emission spectroscopy. For more detail on the methods used, please contact the author.

<b>Name of Sample</b>	<b>Description</b>	<b>Additional Detail</b>
Settling pond water	Water taken from the settling tanks which receive black water from the gasifier	2 to 4 settling ponds and number in figures indicates which settling pond has been sampled
Settling pond sludge	Sludge taken from the bottom of the settling pond	number in figures indicates which settling pond has been sampled
Disposal pond water	Water taken from the end disposal pond for black water waste	Usually located behind, or to the side of, the rice mill or facility
Disposal pond sludge	Sludge taken from the bottom of the disposal pond	Number in figures indicates which disposal pond has been sampled
Water treatment plant water	Water taken from the water treatment facility at site (4)	Only site (4) has a waste water treatment facility
Water treatment plant sludge	Sludge taken from the water treatment facility at site (4)	
Disposal stream water	Water taken from a stream into which black water flows directly from the settling ponds	Disposal streams occur where there is no disposal pond or where the disposal pond is more than 10 m from the settling ponds
Disposal stream sludge	Sludge taken from the bed of the stream into which black water flows directly from the settling ponds	
Pond (with no gasifier waste input) water	Water taken from a pond close by to the gasification facility which is not in receipt of any waste water arising from the gasifier. These other ponds are used for providing baseline measurements.	Several such ponds surveyed appeared to receive other types of organic or nutrient-rich waste, with clear evidence of eutrophication at site 9, for example. In other cases, there was no apparent pollution, e.g. at site 4.

Table 3: Sample Names and Descriptions



Figure 1: Dissolved Oxygen (DO) (hatched columns) and Electrical Conductivity (EC) (black columns) measurements across the nine sites. The black horizontal line shows the threshold for drinking water for EC, acceptable drinking water quality having a *lower* EC than this. The dashed horizontal line shows the threshold for DO in water discharged in a public area or sewer, water of an acceptable quality having a *higher* DO level than this.

Figure 2: Biological oxygen demand (BOD) (Dissolved Oxygen in mg per litre). The horizontal black line indicates the regulatory threshold, above which waste water contains too much pollution.

Figure 3: Chemical oxygen demand (BOD) (Dissolved Oxygen in mg per litre). The horizontal black line indicates the regulatory threshold, above which waste water contains too much pollution.

Figure 4: Concentration of phosphate, nitrate, nickel, lead, iron, copper and chromium in water and sludge samples (solid horizontal bars) where sampled values exceeded regulatory thresholds (shown as Maximum Permissible Level in hatched horizontal bars).

Figure 5: Concentration of total suspended and total dissolved solids (TSS and TDS) (in mg per litre). The regulatory threshold beyond which TSS is considered too high is shown by the horizontal dashed line (80 mg/l), while the solid horizontal line shows the threshold for TDS (2000 mg/l).

Figure 6: Concentration of zinc and manganese in sludge samples (solid horizontal bars) where sampled values exceeded regulatory thresholds (shown as Maximum Permissible Level in hatched horizontal bars).

Figure 7: Concentrations of cresols and phenol in a range of water and sediment / sludge samples collected from six of the sites (units mg/l). The horizontal black line shows the 'intervention concentration' under Dutch regulation for phenol in sediments (14,000 micrograms ( $\mu\text{g}$ ) per litre). The MPLs for cresols in sediments and surface water (5000  $\mu\text{g}$  per litre and 230  $\mu\text{g}$  per litre respectively or ppb) and the MPL for phenols in surface water (2000  $\mu\text{g}$  per litre) are too small to be able to show easily here.

Figure 8: PAH concentrations in waste water and sludge samples from sites 1, 3, 4, 5, 6, 7 and 9. (Units mg/kg dry weight). The regulatory threshold for the PAHs is close to the 'x' axis at 40 mg/kg and is not shown here.

Figure 9: PAH concentrations in waste water and sludge samples from sites 1, 3, 5, 6, 7 and 9 (removing the highest peaks at site 1 and 4). (Units mg/kg dry weight). The regulatory threshold for the PAHs is close to the 'x' axis at 40 mg/kg and is not shown here.

Figure 10: BETX concentration in waste water and sludge samples (units  $\mu\text{g/litre}$  or  $\mu\text{g/kg}$ ).

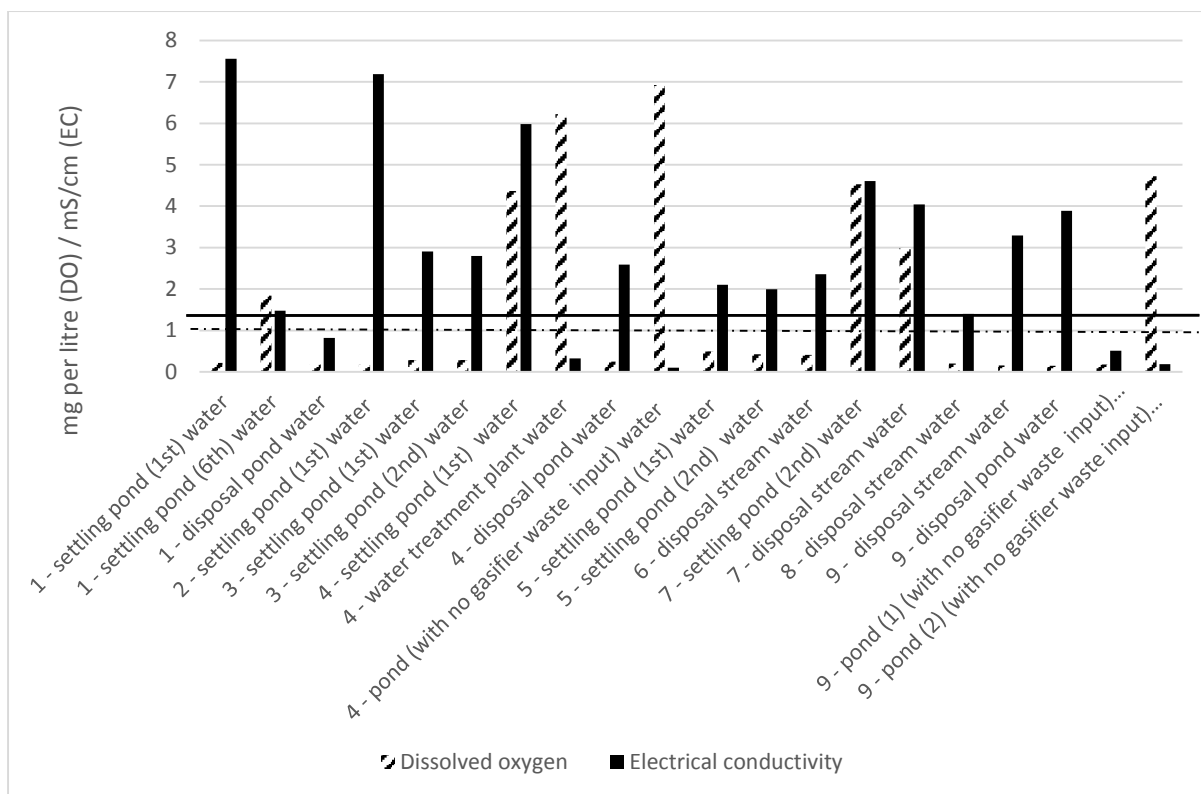


Figure 1

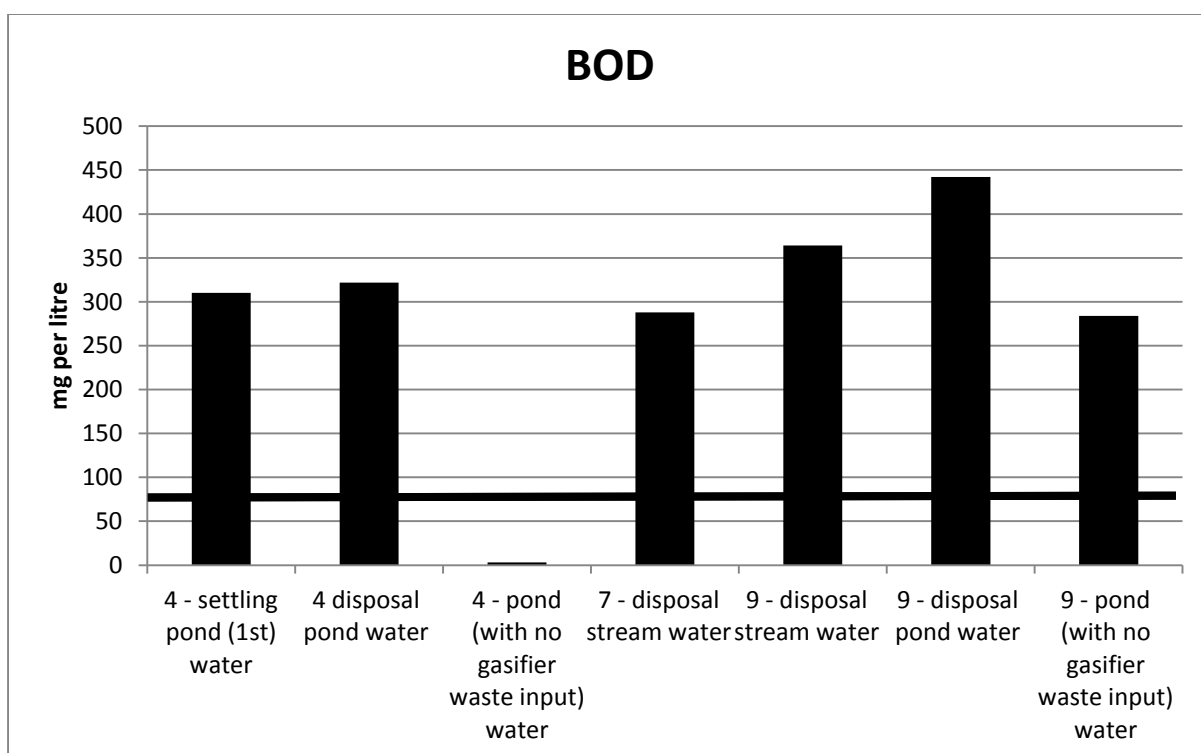


Figure 2

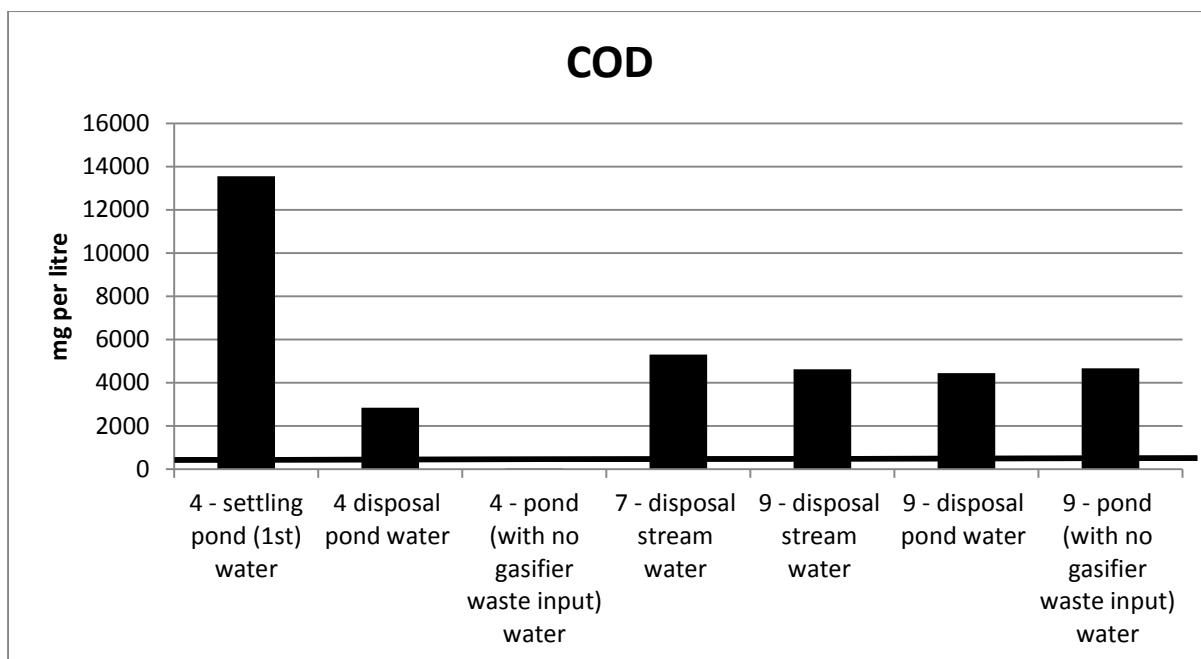


Figure 3

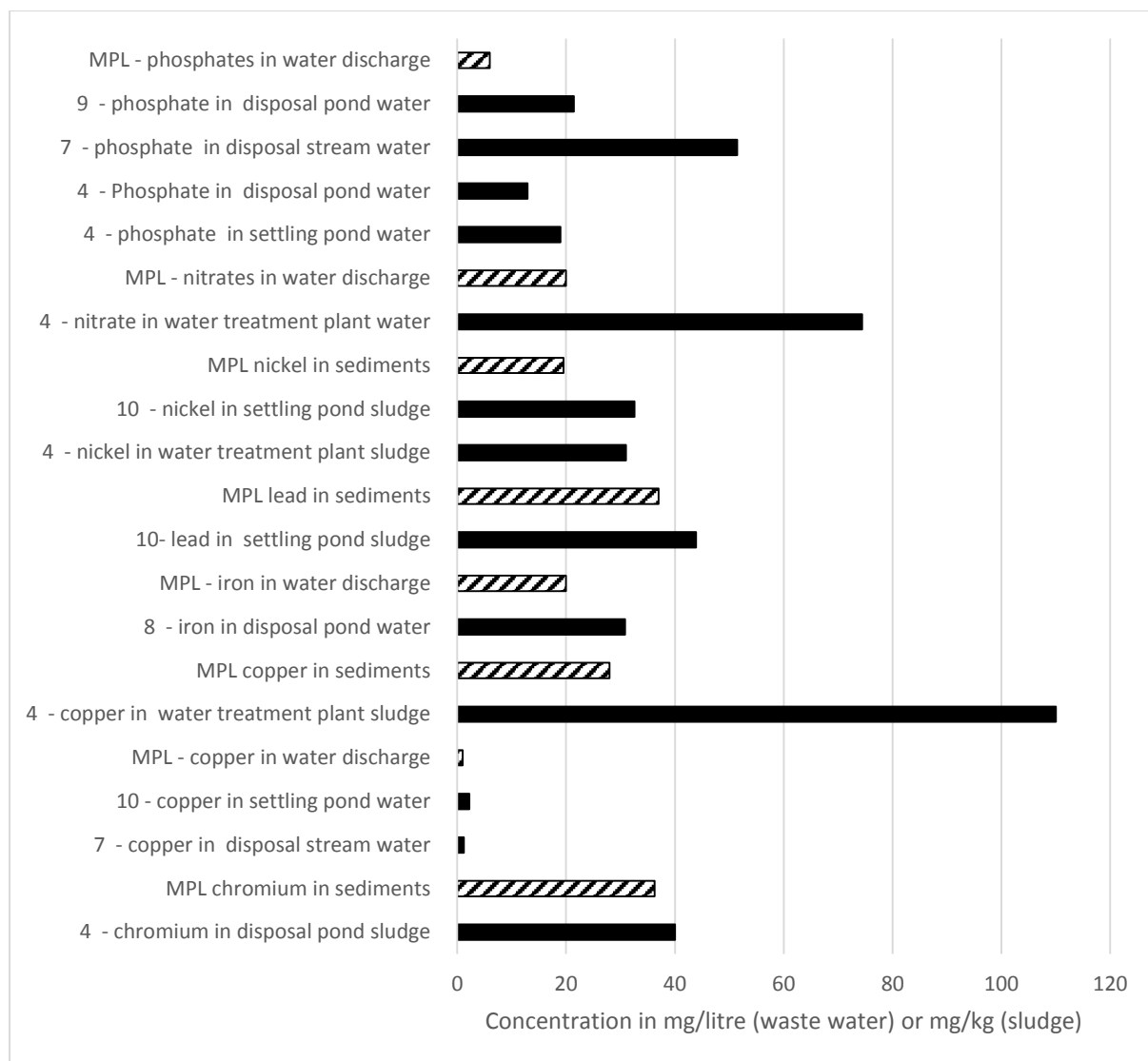


Figure 4

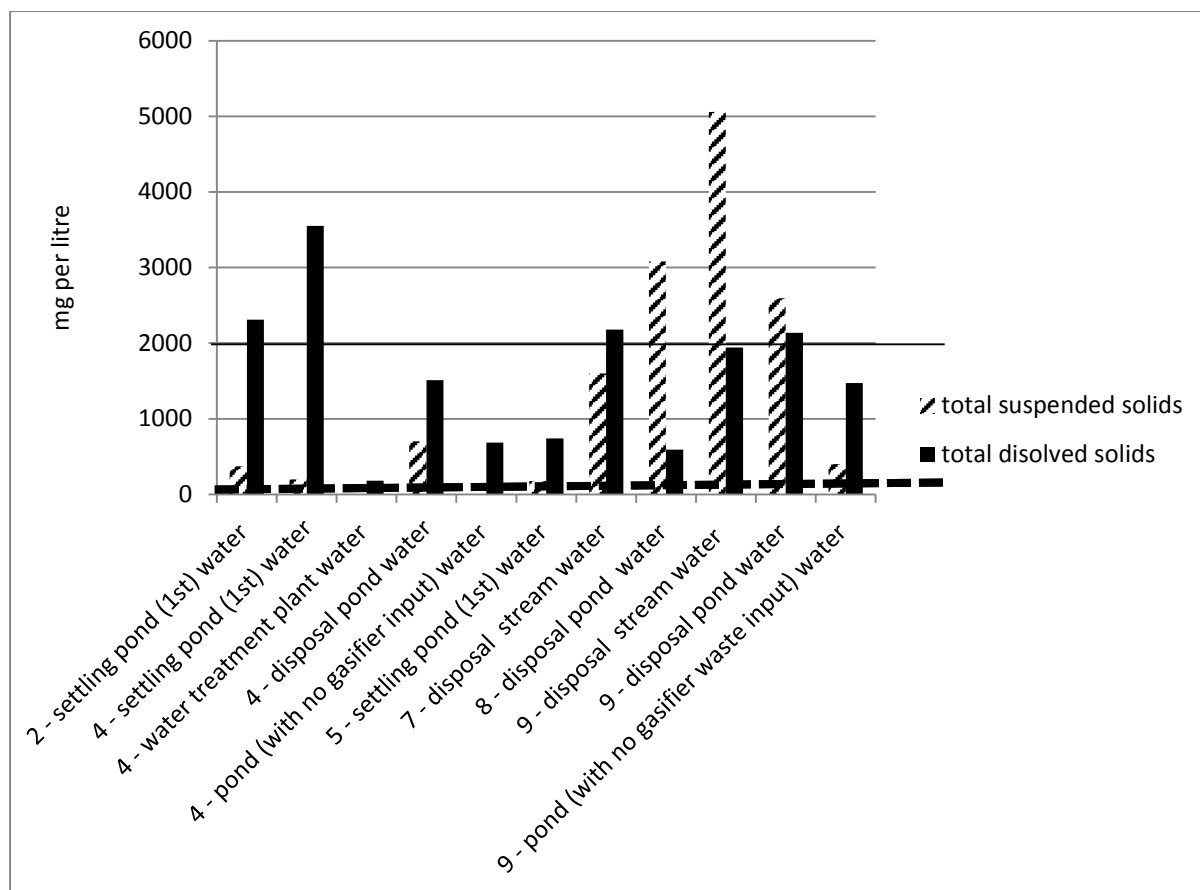


Figure 5

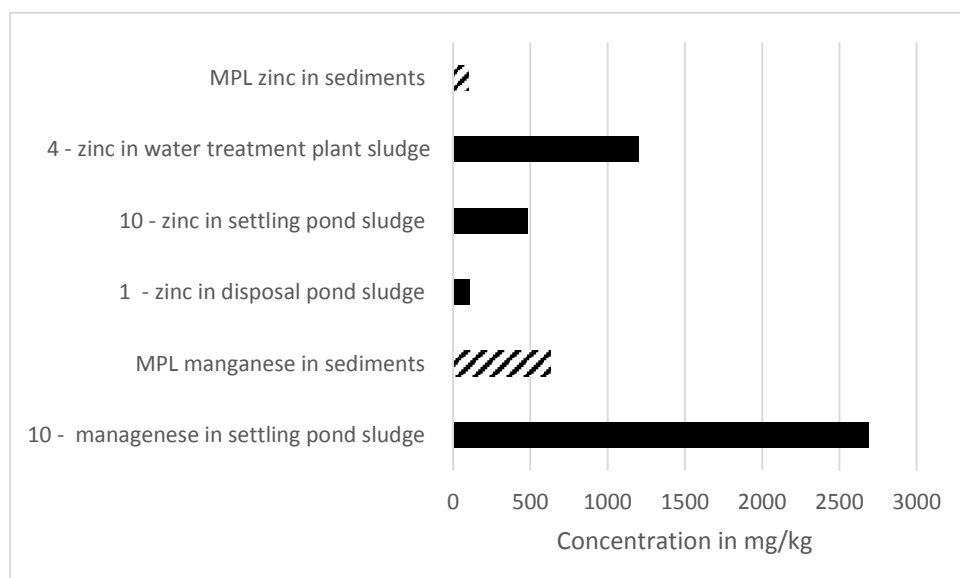


Figure 6

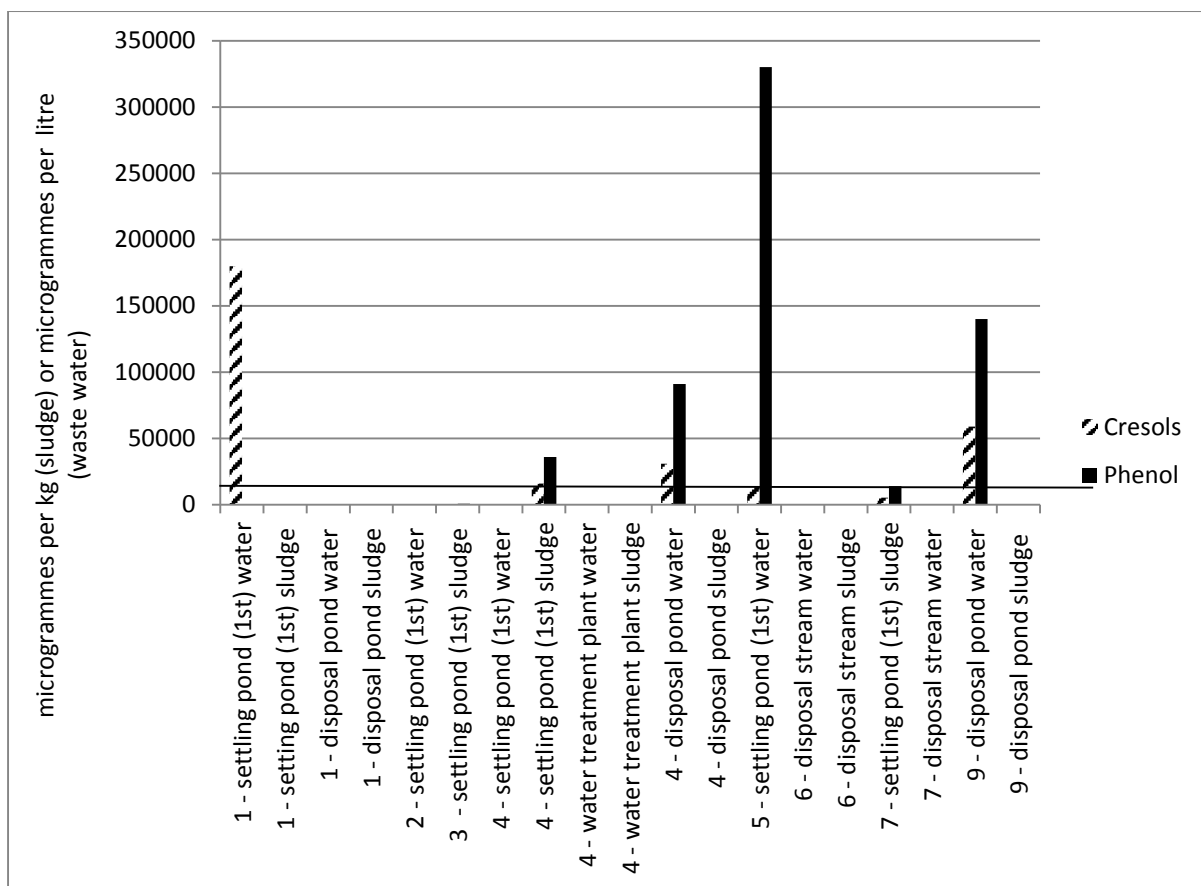


Figure 7

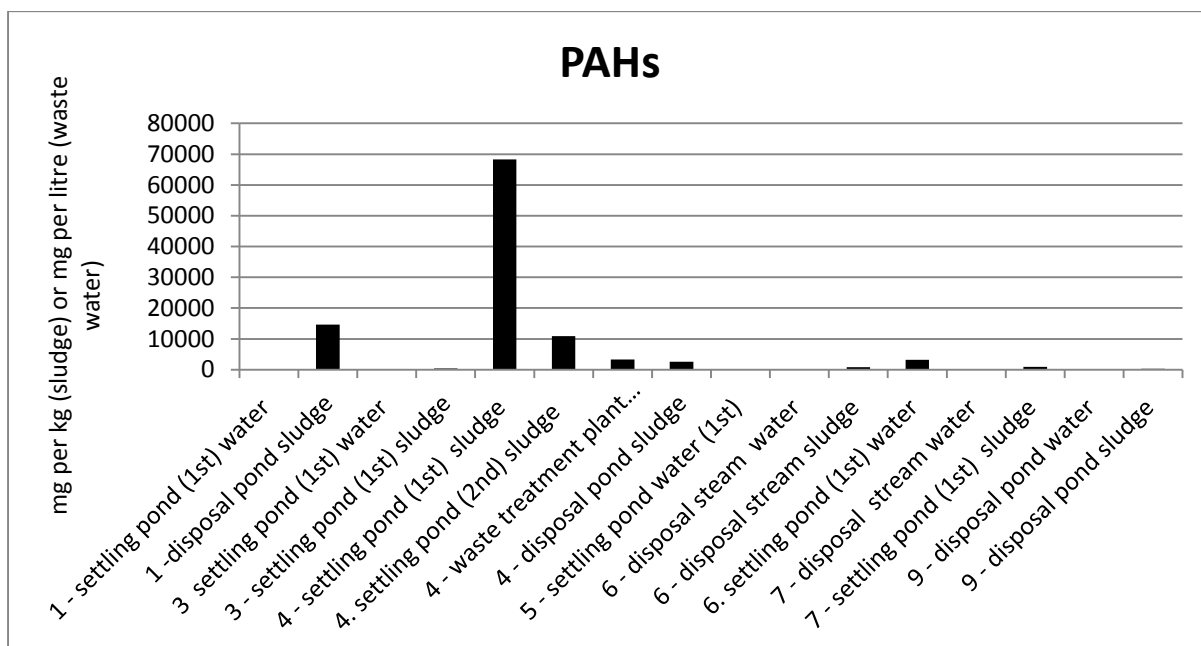


Figure 8

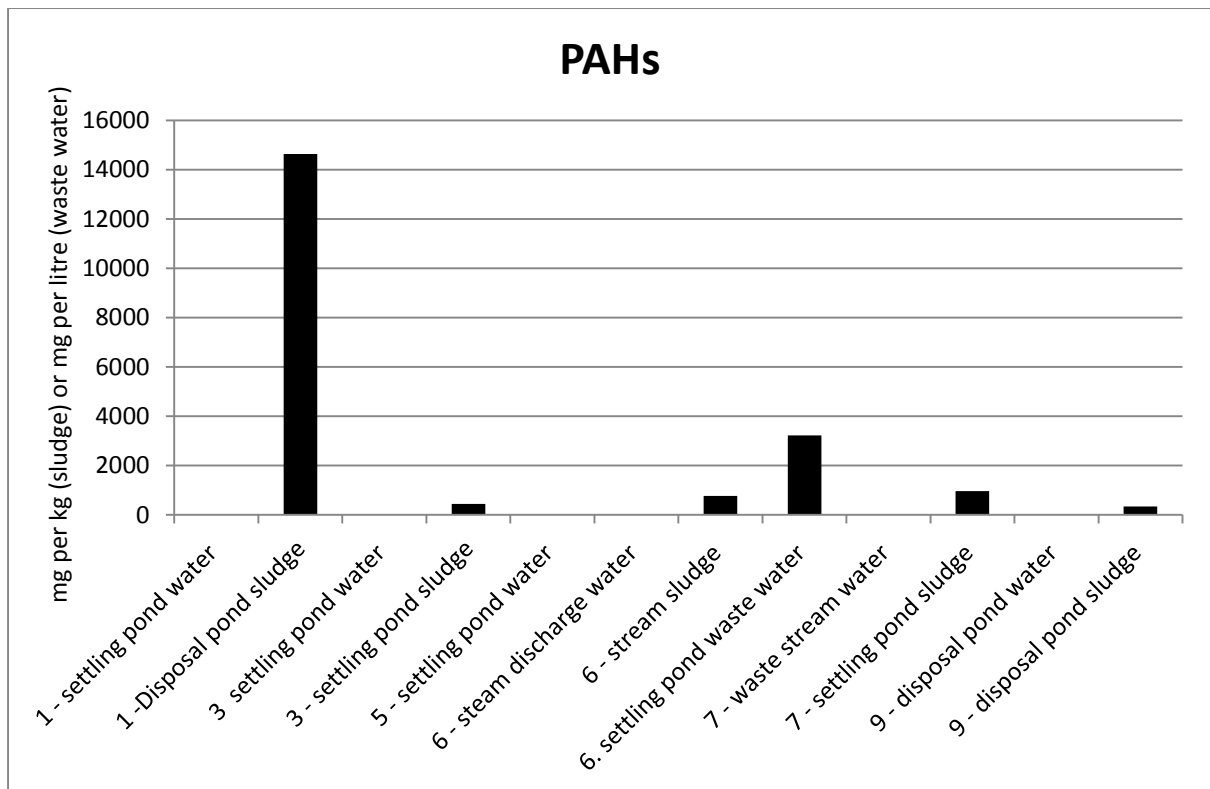


Figure 9

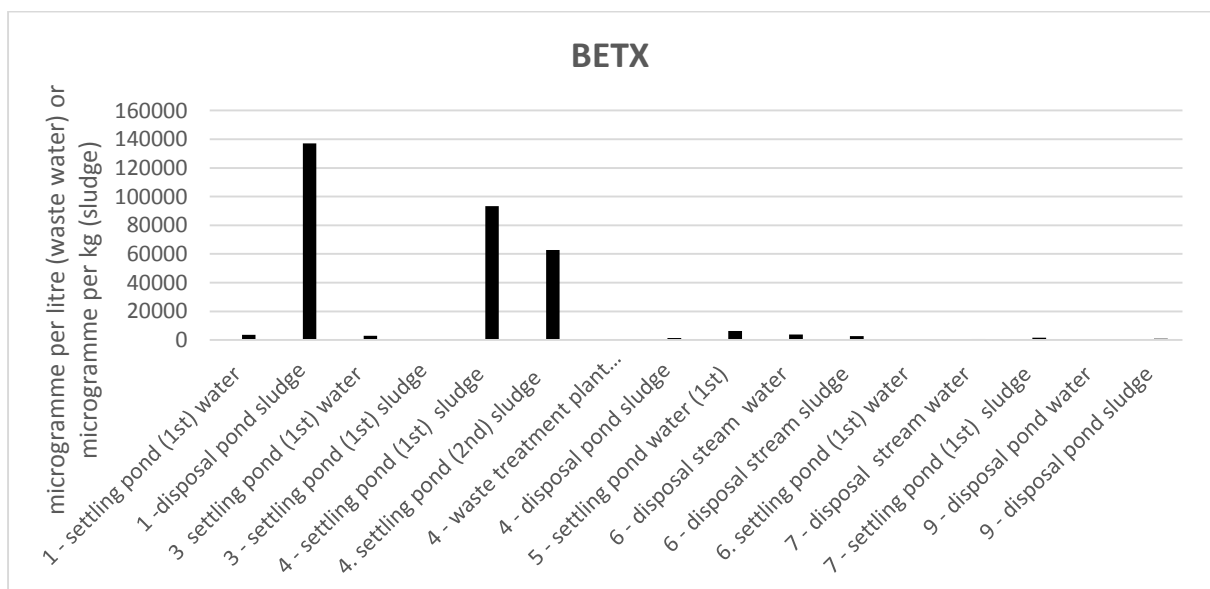


Figure 10

**Key Words:** biomass gasification, rice husk feedstock, waste water, chemical analysis, environmental analysis, black water